Northwest Green Chemistry

The Potential for Generating Inadvertent PCBs through TiO_2 Manufacturing Using the Chloride Process

A white paper prepared for the Spokane River Regional Toxics Task Force

18 February 2019

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Executive Summary

The Spokane River Regional Toxics Task Force (SRRTTF) leads efforts to find and reduce toxic compounds in the Spokane River with an emphasis on polychlorinated biphenyl (PCB) compounds. The SRRTTF contracted Northwest Green Chemistry (NGC) to produce a white paper/memo to learn more about the production of titanium dioxide (TiO_2) and its potential to produce inadvertent PCBs that could end up in consumer and industrial products that could impact the Spokane River. NGC gathered information via reviews of the scientific literature, performed web-based research of trade publications, government publications, and company websites, and interviewed some academic and industry experts.

There is limited evidence that TiO_2 manufactured using the chloride process may produce low levels of PCBs that could be associated with the TiO_2 product. It is not possible to say if these PCBs are at a level of concern until more is known about the range of levels produced, the congeners formed, how the product is used, and how people are exposed. Expert opinion in industry generally holds that PCBs are not expected to be present because the chloride process includes very high temperature unit processes that should destroy organic compounds like PCBs. Therefore testing is not done, and test data are not readily available. However, one pigment and coatings supplier who purchases TiO_2 for use in products shared results from testing two batches of TiO_2 powder from two different manufacturers, and found PCB levels at 85ppb using EPA Method 1668C. Experts also noted that chloride manufacturing processes can vary between companies based on the original technology used, and process improvements made to it over time. This variability may result in different degrees of PCB destruction.

We believe it is not accurate to say that inadvertent PCBs 1) cannot be formed and/or 2) are formed but completely destroyed during high temperature manufacture using the chloride process. Information from the scientific literature and limited test data provide sufficient evidence to warrant further investigation. We recommend testing different grades of TiO_2 manufactured by different suppliers who use the chloride process. We recommend testing the pure pigment, rather than formulated products containing TiO_2 because TiO_2 could pick up PCBs from the ambient environment; and other chemicals used in a formulation could contain PCBs. We also recommend testing both pigmentary and ultrafine (nano) TiO_2. Given the predominant production and use of TiO_2 manufactured using the chloride process, and estimating PCBs at 85ppb in TiO_2, we estimate that 23.6 micrograms of PCBs are associated annually with TiO_2 containing products per capita in the US. This translates to a contribution of 16.2 g/year in the greater Spokane region.

1.0 Introduction

The Spokane River Regional Toxics Task Force (SRRTTF) is a multi-stakeholder initiative organized to lead efforts to find and reduce toxic compounds in the Spokane River (SRRTTF 2018). SRRTTF works collaboratively to characterize the sources of toxics in the Spokane River and to identify and implement appropriate actions needed to make measurable progress towards meeting applicable water quality standards for the State of Washington, State of Idaho, and The Spokane Tribe of Indians, and in the interests of public and environmental health. The Spokane River exceeds the water quality standards for PCBs and dioxins (PCDDs) in several segments of the river.

The SRRTTF is actively working to better characterize the amounts, sources and locations of PCBs and other toxics entering the Spokane River; preparing recommendations to control and reduce those sources, reviewing Toxic and Source Management Plans, and monitoring and assessing the effectiveness of toxics reduction measures.

The SRRTTF commissioned Northwest Green Chemistry (NGC) to produce a white paper/memo to learn more about the production of titanium dioxide (TiO_2) and its potential to produce inadvertent PCBs (iPCBs) that could end up in consumer and commercial products that could eventually impact the Spokane River. NGC gathered information via reviews of the scientific literature and performed web-based research of trade publications, government publications, and company websites. This work was supplemented with interviews of some academic and industry experts. See Appendix 1.

2.0 Production of Titanium Dioxide (TiO_2)

Approximately 6 million metric tonnes (6.6 million US tons) of pigmentary TiO_2 are produced annually worldwide and this number continues to increase. TiO_2 pigment is a global commodity with consumption distributed between paints (including lacquers and varnishes) (60%), plastics (25%), paper (3%), and 'other' (4%). (Maas 2018). Other industry estimates are lower for paints but the ratio relative to plastics and paper is the same. 'Other' uses of TiO_2 include catalysts, ceramics, coated fabrics and textiles, floor coverings, printing ink, and personal care products including cosmetics applied to the skin (including the eye area) and sunscreen. One researcher estimated for a beach in France, which held around 3000 people daily, around 2.2 tons of sunscreen cream was used over the height of summer. Considering reasonably that half of the creams contained 5% titanium dioxide, they estimated that 1.7 kg of titanium dioxide were released per day. They also measured daily concentrations of TiO_2 in the water which ranged from 15-45 micrograms/liter (Goldschmidt, 2018).

TiO_2 is approved by the US Food and Drug Administration (FDA) as a food additive and is found in toothpastes (ChemicalSafetyFacts.org, 2019). The top five global TiO_2 vendors in 2017 were Chemours, CRISTAL, Huntsman, KRONOS and Tronox (Business Wire 2017). China is the primary manufacturer (2.94 million tons) followed by Europe, followed closely by the US (1.36 million tons) (US Geological Survey 2018). Ultrafine (nano) TiO2 is estimated at about 1% of TiO_2 production and manufacturers of pigmentary TiO_2 do not necessarily also manufacture the ultrafine (nano) form.

There are two primary ways to process titanium containing minerals (ilmenite or rutile) into intermediates that are then oxidized into TiO_2. The sulfate (sulphate in British English publications) method involves digesting the mineral in sulfuric acid to generate titanyl sulfate. The titanyl sulfate is then hydrated to form the solid titanium dioxide. The hydrated titanium dioxide is then heated in a furnace ((300K-1000K) depending on the process step, and the desired end crystal structure) to produce anhydrous titanium dioxide. Finally the titanium dioxide is milled down to the desired particle size before being used as a pigment (Kienast 1973) (Essential Chemical Industry 2017). See (Figure 1).

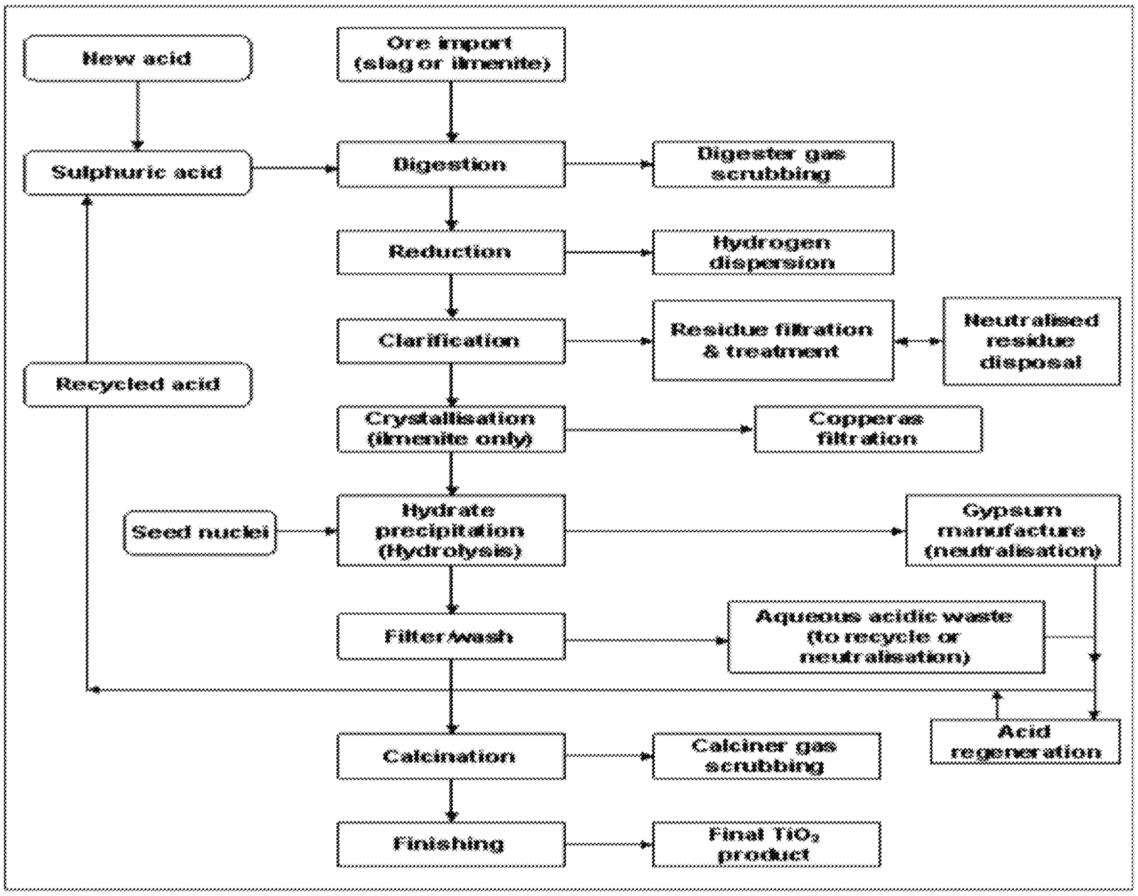


Figure 1. Outline flow diagram – titanium dioxide production by the sulfate process route (European Commission 2007)

The ‘chloride’ method involves reacting the raw mineral with chlorine gas at high temperatures (>1200C) in the presence of coke to produce titanium tetrachloride. The resultant titanium tetrachloride is then burned in the presence of oxygen to produce titanium dioxide. During this step nucleating agents are added and reaction conditions are controlled to give the desired particle sizes for the pigments (Figure 2). See also Appendix 2 for an overview of the TiO_2 chloride manufacturing process provided by CRISTAL.

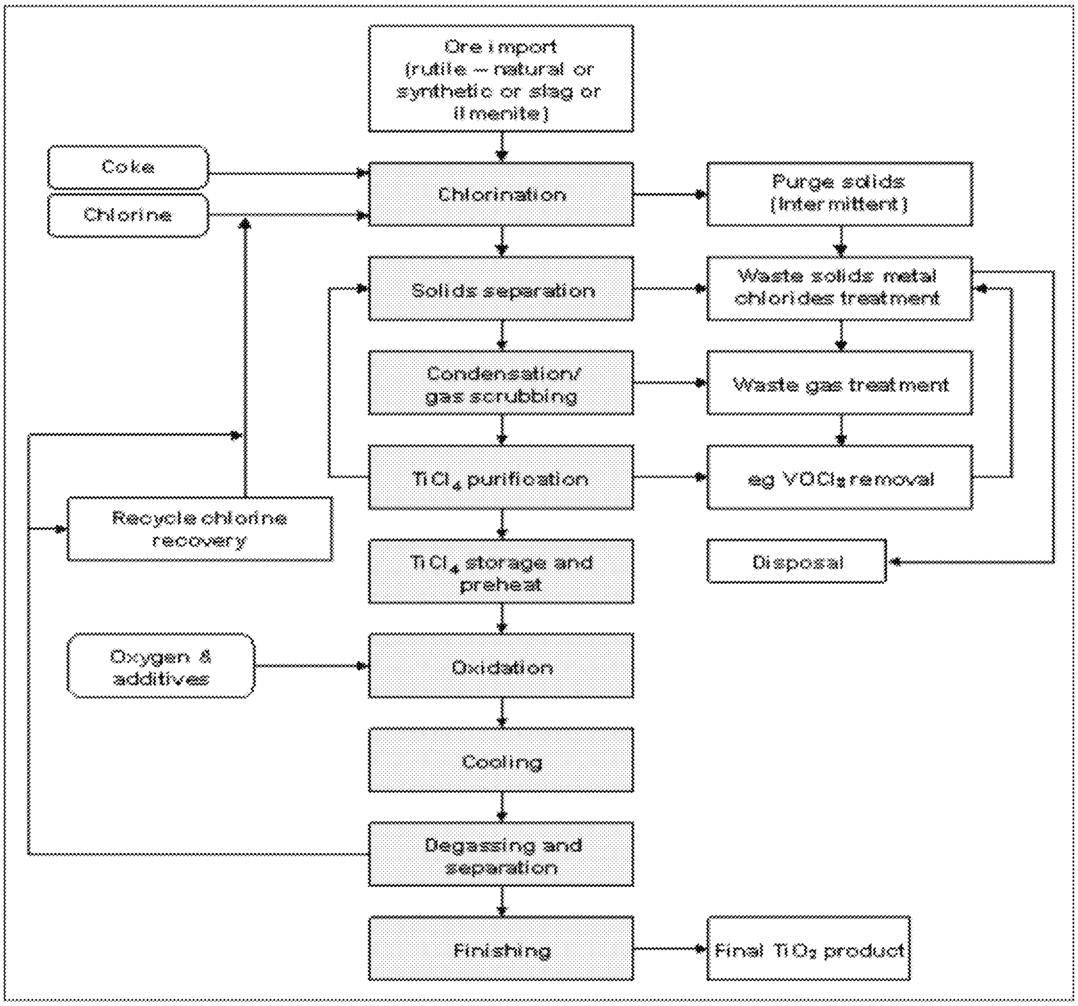


Figure 2. Outline flow diagram – titanium dioxide production by the chloride process route (European Commission 2007)

Alternatively, titanium dioxide particles can be produced by hydrolyzing the titanium tetrachloride in a controlled manner to create ultrafine TiO_2, aka nanoparticles (Cheng 1994). See Figure 3. The difference is due to the use of hydrolysis rather than oxidation for better particle size control.

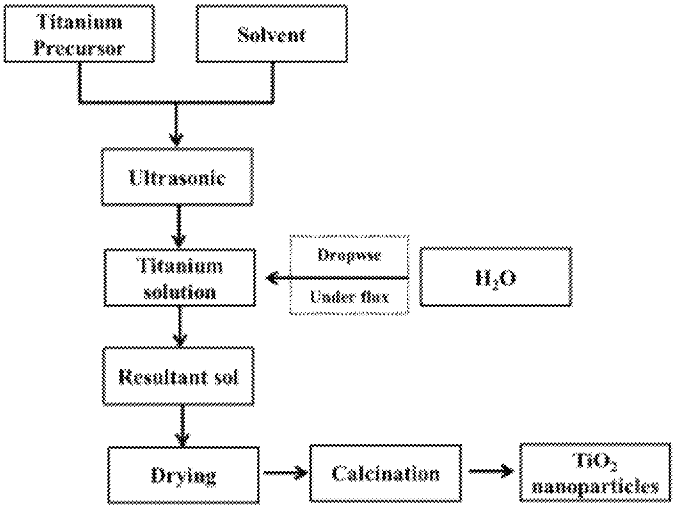


Figure 3. Scheme of the preparation of TiO2 nanoparticles sol-gel (Gupta 2012)

2.1 Relative Use and Benefits of the Chloride versus the Sulfate Process

The sulfate process is the older process of the two, developed in 1916. The chloride process was developed in 1948. Most industry sources state that the use of the chloride process continues to grow worldwide with the exception of China, where new sulfate plants are being built. About 60% of total TiO_2 production is estimated to be from the chloride process with 40% from the sulfate process (Gazquez, 2014). Based on web research and expert interviews, it was determined that the primary, if not exclusive, mode of production of TiO_2 in the US is the chloride process. The primary mode of production in China is the sulfate process. And in Europe, the relative ratio of use of both processes is mixed.

Year	Sulphate process (2)		Chloride process		Total
	kt per year	%	kt per year	%	kt per year
1965	1254	90.3	135	9.7	1389
1970	1499	77.4	437	22.6	1936
1977	1873	72.3	716	27.7	2589
1988	1781	60.2	1178	39.8	2959
1995	1481	46.0	1739	54.0	3220
2000 (1)	1540	40.0	2310	60.0	3850
(1) Estimated; (2) A number of plants based on the sulphate process have recently been commissioned in China.					

Table 1. World production of TiO_2 pigment using the sulfate vs the chloride process in kilotonnes per year (1965-2000) (European Commission 2007)

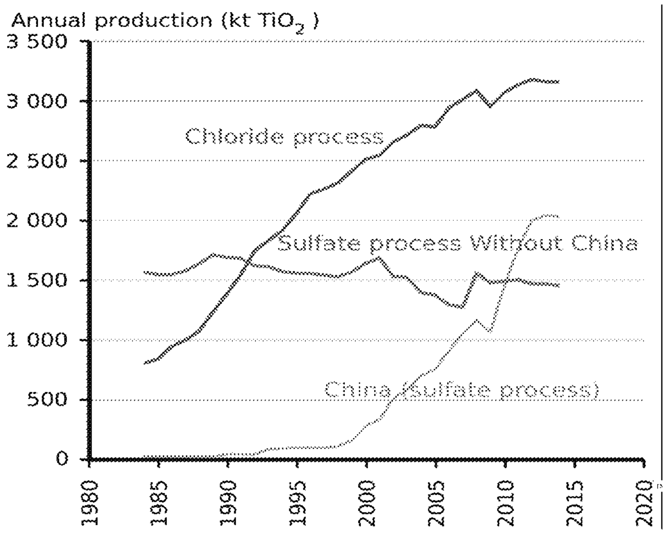


Figure 4. Annual production of TiO_2 pigment using the sulfate vs the chloride process with a focus on China (Borvan53 2015)

The sulfate process is considered less environmentally friendly because of the acid wastes that are generated. However, this may not fully address issues of toxicity that arise with wastes associated with the chloride process (Essential Chemical Industry 2017).

Sulfate Process	Chloride Process
long established and simple technology	new technology
uses lower grade, cheaper ores	needs high grade ore
batch process	continuous process
large amounts of waste materials	small amounts of waste formed with toxicity problems: Cl_2 and $TiCl_4$
pollution control expensive	recovery and recycling of chlorine possible
produces anatase and rutile pigments	only produces rutile pigments

Table 2. Comparing the sulfate and chloride processes (Essential Chemical Industry 2017)

3.0 Feasibility of Generating Inadvertent PCBs

The basic chloride process for producing TiO_2 is presented in Appendix 1. The process is designed to purify TiO_2. The first step is chlorination where the ore and chlorine are combined to form titanium tetrachloride. Along with the $TiCl_4$, other metal chlorides are formed. The next step is condensation and purification. Lowering the temperature allows for the separation of the metal chlorides from the $TiCl_4$ which is then converted to TiO_2 by reaction with oxygen. Ultrafine (nano) TiO_2 is obtained by using hydrolysis rather than oxidation, which allows for better control of particle size and properties. The presence of organic carbon and chlorine can lead to the formation of highly chlorinated PCBs. Sufficiently igh temperature processes can destroy PCBs. The resulting presence or destruction of PCBs may depend on the nuances and efficiencies of the manufacturing process steps.

3.1 Scientific research testing commercial mixtures

Hu and Hornbuckle (Hu 2009) measured PCBs in paint pigments from three different paint retailers accounting for about 70% of the market share in the United States. They extracted the pigments using modified EPA Method 3545 and then tested for PCBs using gas chromatography with mass selective detection (GC-MS/MS) modified from the EPA Method 1669A. They reported that no PCBs were found in inorganic pigments that primarily contain titanium dioxide, iron oxide, raw umber, or carbon black. They did however find PCBs in two groups of organic pigments, azo pigments and phthalocyanine pigments. The authors did not provide information on the composition of the white pigments they tested and assumed to contain titanium dioxide. The source and concentration of titanium dioxide in the pigments was unknown.

Researchers in Germany (Ctistis et al. 2016) obtained titanium pigment from a retailer in the Netherlands (verftechnieken.nl). The researchers measured for PCBs, polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) using German standard methods for the examination of water, wastewater, sludge and sediments. They found total PCBs in the pigment at 2.7 ppb (2680 ng/kg) and a congener distribution as presented in Figure 5.

Fig. 2 PCB congener distribution (in relative mass percentage %) and corresponding mass concentrations in nanograms per kilogram found in the commercial TiO_2 sample A. The dioxin-like PCBs are indicated in *red* (sample descriptions are included in the "Experimental part" section)

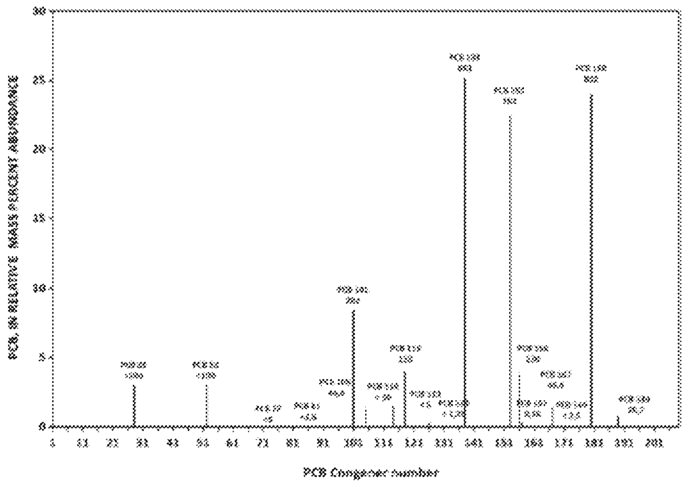


Figure 5. PCB congener distribution and mass concentrations in commercial titanium white pigment (Ctistis 2016)

As with the research by Hu and Hornbuckle, the authors did not provide information on the chemical constituents in the pigment. The source and concentration of titanium dioxide in the pigments was unknown.

3.2 Expert opinion

NGC staff met with several industry and academic experts to better understand the potential for forming inadvertent PCBs in the TiO_2 manufacturing process. These interviews included experts from three of the five largest global TiO_2 manufacturing corporations. See Appendix 2 for the list of interviewees.

All three of the major manufacturers shared that they do not test for PCBs in their TiO_2 product because they do not expect to find them, mostly due to the very high temperatures used in production that would cause the PCBs to decompose.

One expert from a major TiO_2 manufacturing corporation claimed that PCBs are formed in the chloride process but they are destroyed at the high temperatures used to produce the $TiCl_4$ and potentially also during the subsequent oxidation process. This expert also noted that it is possible for TiO_2 pigments once produced and sold, to pick up PCBs from the ambient environment at very low levels since it is very difficult to find any environment that is truly free of PCBs. This expert also noted that PCBs in products that contain TiO_2 may also come from other chemicals used in product formulations. Another expert noted that PCBs are being found in silicones used in paints and coatings, the dominant use of pigmentary TiO_2. Based on preliminary research, the silicones most likely to contain iPCBs are those synthesized from phenyl siloxanes.

Experts from a second large TiO_2 manufacturer claimed that because the TiO_2 process is entirely inorganic, it is not possible to produce organic compounds such as PCBs. That the process is entirely inorganic seems unlikely given that ore and coke are used and these materials may contain organic matter. However, we do not have insight into the manufacturers proprietary process and feedstock. They recommended that the research team review the EU Commission BREF document (European Commission 2007). The research team reviewed the document released by BREF and found reference to estimated emissions of 0.00041 - 0.00025kg of chlorinated organics per /tonne of TiO_2 generated using the chloride process in 1999-2002.

	kg/tonne 1999	kg/tonne 2000	kg/tonne 2001	kg/tonne 2002
Discharges to water				
Hydrochloric acid	16	13	13	12
Titanium (Ti)	0.8	0.6	0.5	0.6
Suspended solids	0.6	0.5	0.4	0.5
Manganese (Mn)	0.6	0.6	0.4	0.5
Iron (Fe)	0.28	0.55	0.67	0.61
Vanadium (V)	0.03	0.03	0.03	0.02
Chromium (Cr)	0.003	0.004	0.004	0.002
Zinc (Zn)	0.006	0.007	0.009	0.005
Nickel (Ni)	0.019	0.015	0.004	0.001
Lead (Pb)	0.011	0.009	0.002	0.000
Copper (Cu)	0.003	0.003	0.006	0.001
Arsenic (As)	0.0001	0.0001	0.0001	0.0000
Cadmium (Cd)	0.00018	0.00013	0.00012	0.00001
Mercury (Hg)	0.00007	0.00001	0.00000	0.00000
Chlorinated organic compounds	0.00041	0.00027	0.00025	0.00025
Emissions to air				
Carbon monoxide	181	116	65	83
Carbonyl sulphide	3.2	1.9	1.3	0.4
Nitrogen oxides (as NO_2)	1.2	1.3	1.2	1.2
Particulates	0.4	0.1	0.1	0.1
Sulphur dioxide	0.3	0.2	0.1	0.1
Hydrogen chloride	0.2	0.0	0.0	0.0
Chlorine	0.00041	0.00054	0.00050	0.00012
Hydrogen sulphide	0.1	0.1	0.0	0.0
Carbon dioxide (ex process)	437	487	729	576
Carbon dioxide (ex combustion)	1304	1090	1110	989
Carbon dioxide (from bought in energy)	609	588	561	540
Wastes to land				
Non-hazardous waste	729	785	881	962
Hazardous waste to land/incineration	0.5	1.8	0.9	1.8
Resource consumption				
Water usage m^3	38	32	31	32
Energy usage GJ	29	26	26	23

Table 3. Summary of emissions (1999-2002) in the Grantham Works TiO_2 plant (chloride process) (European Commission 2007)

While the term chlorinated organics does not necessarily imply production of PCBs, it does demonstrate that production of chlorinated organic wastes or emissions can occur at least at some point in the chloride TiO_2 manufacturing process.

A third manufacturer confirmed that PCBs are generated in the chloride TiO_2 manufacturing process and that they may or may not be fully destroyed depending on the technology used by the manufacturer. They shared that while all chloride manufacturing is similar at the conceptual level, each company continues to improve its specific process technologies; and some processes are likely to be better than others for destroying PCBs. Most big changes in process technologies occur around the chlorination and oxidation steps; the steps that are most relevant to PCB production (Ctistis 2016).

Very low levels of PCBs in TiO_2 powder were measured by a manufacturer of color pigment and coatings who purchases pigmentary TiO_2 for use in other products. This manufacturer obtained two batches of raw TiO_2 powder, produced by two different sources, to screen for compliance below regulatory limits. The samples were taken directly from the manufacturers bag, with no special handling, and tested for PCBs using EPA Method 1668C. Both batches were found to contain 0.085 ppm (85ppb) PCBs. The manufacturer reported that no one congener stood out as higher than the others. However, as a family, the tri-chlorinated congeners were identified at higher levels followed by the tetra- and penta- chlorinated congeners.

Method 1668C is the standard method used in the industry for detecting PCBs (HRGC/HRMS 2010). Prior versions of Method 1668C, which revised the upper recovery limit acceptance criteria for some congeners, were 1668B (January 2009), which changed the single lab acceptance criteria to inter-laboratory criteria and the original 1668A (December 1999) (HRGC/HRMS 2010).

3.3 Estimated levels of production of inadvertent PCBs

An estimate of global TiO_2 production in 2017 was 6 million metric tonnes. If one uses estimates that 60% of the production is based on the chloride process, then about 3.6 million metric tonnes of chloride-based TiO_2 were produced.

If the TiO_2 produced via the chloride process contained 85 ppb PCBs, then the annual global production of PCBs would be 3.6 million metric tonnes x $85/1x10^9$ which is 0.306 tonnes (0.301 US tons, 675 pounds, 30600g) of PCBs

If one estimates that about 15% of global TiO_2 is used in the US and essentially all of it is produced via the chloride process then, 0.15 x 6 million metric tonnes = 0.9 million metric tonnes which is about 25% of the total TiO_2 produced using the chloride process. If the TiO2 contained PCBs at 85ppm, then the total PCBs associated with TiO2 used in the US would be about 169 pounds or ~7700g.

The population of the US is approximately 325.7 million so the annual per capita contribution is 2.36×10^{-5} g (23600 nanograms) per person. The population of the Spokane/Spokane Valley/Coeur D'Alene region is about 685,000 so the potential regional total contribution of PCBs in TiO_2 used in a variety of products each year is about 16.2g of PCBs.

This number should be considered as a worst-case scenario and may not reflect actual releases. While products such as sunscreen can result in direct discharge of TiO_2 to water bodies such as the Spokane River (Goldschmidt, 2018), other products such as plastics and coatings may retain the TiO_2 and associated PCBs in the product matrix, delaying or retarding direct environmental releases. In addition, different grades of TiO_2 are used for different applications. It would be useful to better understand which, if any, grades of TiO_2 are more likely to contain PCBs, how those grades are used in products, and the associated exposure profiles.

4.0 Summary and Recommendations

There is evidence that TiO_2 manufactured using the chloride process may produce low levels of PCBs that may be associated with the product. It is not possible to say whether or not these PCBs are at a level of concern until more is known about what the levels are, what the congeners are, how the product is used, and how people and the environment are exposed. While expert opinion in industry holds that it is not necessary to test for PCBs because they are not expected to be present, there is need for testing to better understand the concentration ranges of PCBs that may be formed.

Based on our findings to date, we expect that levels in the parts per billion range will be found. With only two test data points (both reporting 85ppb) available at this time, we are not able to define the relevant ranges that can be expected. Expert opinion posits that some chloride technologies will result in negligible (non detectible) levels of PCBs. However, we believe it is not accurate to say that inadvertent PCBs 1) cannot be formed and/or 2) are formed but completely destroyed during high temperature manufacture using the chloride process.

This report is intended to support SRRTTF efforts to identify and reduce toxic compounds released to the Spokane River by researching the potential for inadvertent PCBs to be found in TiO_2 manufactured using the chloride process, the levels of PCBs that may be formed, and the ability of industry to keep PCB levels to negligible levels through advanced technology. We believe there is limited but sufficient evidence from the scientific literature, expert interviews and the results of analytical testing by a manufacturer of color pigments and coatings to warrant further investigation. Testing would help resolve the question of the degree to which pigmentary and ultrafine (nano) forms of TiO_2 may contain inadvertently generated PCBs. Prioritizing resources for this testing is up to the discretion of the SRRTTF. Additional work is recommended to better understand how the potential levels of PCBs in TiO_2 compare to concentrations of other sources of legacy and inadvertent PCBs currently being generated or released.

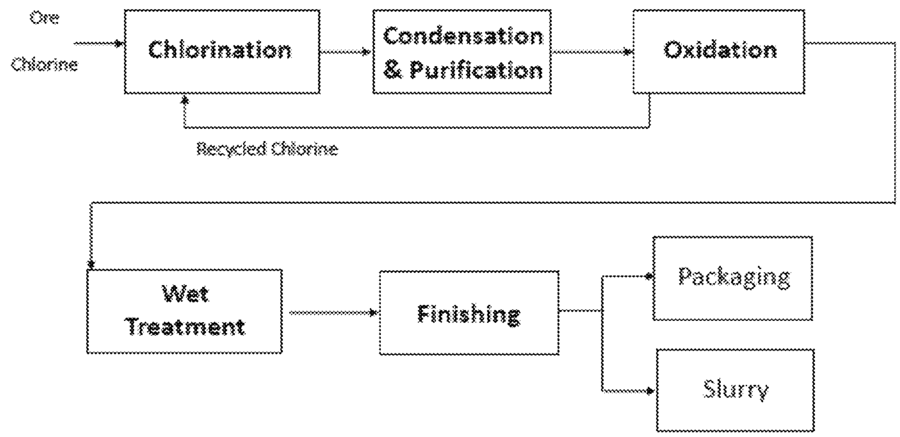
We recommend testing:

1. Both pigmentary and ultrafine (nano) forms of TiO_2 for inadvertent PCBs to confirm if, and how much, inadvertent PCBs are produced using the chloride process. Because ultrafine TiO_2 is typically produced with hydrolysis instead of oxidation for better particle size control, testing should be done separately for both forms.
2. Multiple grades of TiO_2 because different grades undergo variations in process and have different expectations for purity.
3. TiO_2 manufactured by multiple manufacturers. Manufacturers have evolved proprietary processes to improve performance and purity and there may be variability between manufacturers.
4. Pure pigment obtained directly from the manufacturer. We do not recommend testing formulated products containing TiO_2 because TiO_2 could 1) pick up PCBs from the ambient environment during handling and transport, and 2) other chemicals used in the formulation could contain PCBs or dilute the evidence of PCBs from TiO_2.
5. Samples of TiO_2 produced using the sulfate process. This would be a useful control.

5.0 Appendices

Appendix 1: Basic Chloride Process Overview

Chloride Process TiO_2 Technology
Process Schematic



Basic Chemistry - Chlorination

Chlorination Reaction

$$2TiO_2 + 3C + 4Cl_2 \text{ -----> } 2TiCl_4 + CO_2 + 2CO$$

(Approximately)

Typical Chlorination Conditions

- Bed Temperature: 950 - 1100°C
- Bed Composition: Coke 10 to 30%
- Titanium materials: 20 to 55%
- Inert materials: remaining %
- Outlet Temperature: 850 - 1000°C

Condensation & Purification - Purpose

- Cools the gas stream
- Condenses gaseous TiCl4
- Recovers and collects liquid TiCl4
- Removes solids from Main Process
- Segregates crude TiCl4 streams
- Removes entrained solids
- Removes metal chlorides (Fe, V, Zr, Sn)
- Removes Vanadium (VCl_4 & $VOCl_3$)

Oxidation - Purpose

- React $TiCl_4$ with Oxygen
  $TiCl_4 + O_2$ -----> $TiO_2 + 2Cl_2$
- Produce pigmentary TiO_2
- Release Cl_2 for recycle to chlorination
- Separate TiO_2 product from recycle gas stream
- Produce TiO_2 slurry for Finishing

Typical Oxidization Conditions

- $TiCl_4$ vaporizer discharge temp: 400°C
- O_2 preheater discharge temp: 950°C
- $AlCl_3$ discharge temp: 450°C
- "Wet air" temp: 1450°C

Appendix 2: Individuals Interviewed

University:

Rutgers University: Lisa Rodenburg

TiO_2 Manufacturers:

CRISTAL; Doug Herrmann; Mark Pomponi

KRONOS: Kevin Lombardozzi, Olaf Schulze

Chemours: Michael Ober

Pigment and Coating Manufacturers:

Clariant: Romesh Kumar

Color pigment and coating manufacturer (anonymous)

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